Balloon-Borne Observations of Mid-Latitude Fluorine Abundance

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Volume mixing ratio profiles of organic ($CFCl_3$, CF_2Cl_2, CHF_2Cl, $CF_2ClCFCl_2$, CF_4, SF_6) and inorganic (HF, COF_2) fluorine species have been derived from a series of high-resolution infrared solar spectra recorded by the JPL Mk IV interferometer during a September *1993* balloon flight from Ft. Sumner, New Mexico *(34° N; 104° W)*. The total fluorine budget over the 6-39 km altitude range has been evaluated by adding these individual measured profiles to model predictions for the unmeasured inorganic gas COFCl (considered to be at most 6% of the total inorganic fluorine budget). The mean total inorganic fluorine above 35 km was found to be 1.34 ± 0.06 ppbv (parts per billion by volume.), in agreement with the value (1.32 ppbv) inferred from a time-dependent, two-dimensional model. The results for total fluel ine indicate a steady decrease of its volume mixing ratio, with increasing altitude, from a tropospheric value of about 1.88 ppbv to 1.17 ppbv at, *40* km. The autumn 1993 stratospheric budget of inorganic fluorine is commensurate with tropospheric values of fluorine concentrations reported in the late! 1980's. Therefore, the "mean age" of the stratospheric airmass estimated from the MkIV fluorine budget (5-6 years) is in good agreement with model simulations (5-7 years) and recent ATMOS measurements.

INTRODUCTION

The atmospheric lifetimes of most chlorofluorocarbons ((NW'S) and hydrofluorochlorocarbons (HCFC's) are sufficiently long to allow them to be transported to the stratosphere where their chlorine atoms are removed, and then participate in the catalytic destruction of ozone. Estimates of their concentrations in the stratosphere are therefore required to accurately predict their future impacts and hence determine the emission reductions necessary to stabilize present amounts.

Removal of fluorine atoms from CFC's and HCFC's is more difficult than chlorine and so the fluorine are generally released in the later stages of the breakdown and at higher altitudes. Unlike atomic chlorine and bromine, the reactions of atomic fluorine with CH_4 and H_2O are very fast and fluorine is thus efficiently removed to form hydrogen fluoride (HF) and therefore dots not participate in any catalytic cycle that significantly depletes ozone [*Stolarski and Rundel*, 1975]. HF is immune to attacks by stratospheric free radicals, except for the highly reactive and very trace species $O(^1D)$, and radiation less than 165 nm wavelength and therefore cannot be recycled back to active fluorine. Furthermore, HF's insolubility in sulfuric acid makes it incapable of participating in heterogeneous reactions producing active F-containing species [*Hanson and Ravishankara*, 1992] and is generally believed not to lead to catalytic ozone destruction. Recent discussions on the production of CF_3 radicals from HCFC decomposition and its potential to catalytically destroy ozone, analogous to the OH and HO_2 reactions with ozone, have also been demonstrated to be negligible [Ko et al., 1 994].
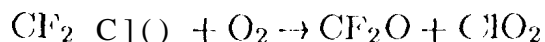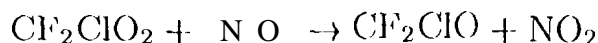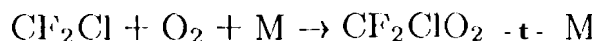
The CFC's and HCFC's are strong mid-infrared absorbers and can cause significant radiative forcing of the surface-troposphere system. Coupled with other long-lived and '(well-lnixd" greenhouse gases ($CO_2, CH1_4, N_2O$, etc.) the change in net irradiance at the tropopause between the years 1980-1990 was about 0.45 w in2, almost four times bigger than the cooling caused by stratospheric ozone depletion during the same period [*WMO*, 1 994]. Long-term decrease of lower-stratosphere temperature have recently been reported [*WMO*, 1 994] and changes in the radiative properties of the stratosphere are an important part of the cause of the trend. Studies have also shown that the globally-averaged warming is most sensitive to (i) the magnitude of the cooling in the lower Stratosphere due to ozone loss, and (ii) the global relative efficiency of bromine for ozone loss as compared

to chlorine [*Daniel et al., 1* 994]. The future radiative forcing and hence climate changes will thus depend upon the time-dependent mix of anthropogenic source gases in the stratosphere. Measurements of F- containing species in the stratosphere uniquely reflect the amounts of anthropogenic gases transported into the middle atmosphere and available for participation in (i) the catalytic destruction of ozone, (ii) the indirect cooling of the lower-stratosphere due to ozone loss, and (iii) the direct heating of the troposphere through infrared absorption.

The purpose of the paper is to describe in detail the MkIV measurements of fluorine species in the troposphere and stratosphere. We first review the chemical degradation of CFC and HCFC in the atmosphere to]-c-affirm that inorganic fluorine species in the stratosphere reflect the amounts of anthropogenic source gases broken down in the middle atmosphere. We then describe the balloon flight on which the solar observations were performed and the technique used to determine slant column abundances and volume mixing ratio (vmr) profiles. Results for the individual flourine-bearing gases are compared with previous measurements and collated in terms of their contribution to the fluorine (organic and inorganic) budget in the atmosphere. Finally, the MkIV measurements of total fluorine abundance in the atmosphere are compared with 2D model simulations and ATMOS measurements.

o11;h41STR% OF STRATOSPHERIC FLUORINE

The release of fluorine from the CFC's is believed to be analogous to the well-known CH_4 oxidation scheme. CFC oxidation in the stratosphere occurs with the break of a C-Cl bond and continues with the breaking of the remaining C-Cl 1)01)(1s before any of the C-F's [*Kaye et* d., 1991]. In Case of HCFC's, the c-c] bonds break after the C-H bond but before any of the C-F do. For CFC's (and HCFC's) containing more than one fluorine atom, source gases are first broken down to CF_2Cl (e.g. $CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$; $CHF_2Cl + OH \rightarrow CF_2Cl + H_2O$) which then undergoes the following chain of reactions

$$CF_2Cl + O_2 + M \rightarrow CF_2ClO_2 + M$$
$$CF_2ClO_2 + NO \rightarrow CF_2ClO + NO_2$$
$$CF_2ClO + O_2 \rightarrow CF_2O + ClO_2$$

The temporary reservoir COF_2 is quite stable and s only slowly broken down by photolysis:

$$CF_2O + h\nu \rightarrow CFO + F$$
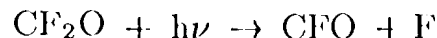
The 1" atoms produced by the reaction chains quickly reacts with H_2O or CH_4 to produce HF.

Source gases with a single fluorine atom are initially broken down to $CFCl_2$ (e.g. $CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$) which then undergoes a similar chain of reactions

$$CFCl_2 -i- O_2 + M \rightarrow CFCl_2O_2 + M$$
$$CFCl_2O_2 + NO \rightarrow CFCl_2O + NO_2$$
$$CFCl_2O + O_2 \rightarrow CFClO -t\ ClO_2$$
$$CFClO + h\nu \rightarrow CFO +-\ cl$$
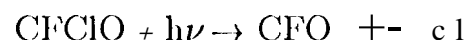
The CFO produced from this, and the previous, reaction chain reacts with O_2

$$CFO + O_2 \rightarrow CF(O)O_2 \rightarrow FO + CO_2$$

to form FO. The fluorine atom is removed from FO by its reaction with $O(^1)$ $(FO + O(^1D) \rightarrow F +- O_2)$.

The remaining fluorine-containing source gas of importance, from the emission scenarios, is $CF_2ClCFCl_2$ (CFC-1 1 3) and is lost via photolysis and reactions with $O(^1D)$. Therefore, measurements of individual fluorine species is uniquely valuable for investigating the atmospheric circulation and the chemical partitioning of this halogen when evolving from source to temporary reservoir to sink in the lower stratosphere.

Instrument And Balloon Measurements

The latest in a series ofFrJ'11/ spectrometers designed at J 1'1,, the MkI V Interferometer [*Toon,* 1 991] uses the solar absorption technique to remotely measure the atmospheric composition. The high spectral resolution $(0.01 cm^{-1})$ and broad spectral coverage $(650-5650\ cm^{-1})$ of the MkIV instrument allows it to measure a large number of different gases simultaneously in the same airm ass. MkIV uses two cryogenically co oled detectors, a HgCdTe photoconductor for wave-numbers below 1 850 cm^{-1}, and an InSb photodiode for wave-numbers above 1850 cm^{-1}. This arrangement prevents photon noise from high wave-numbers degrading the signal at lower wave numbers. Typically, a pair of million point interferograms

take $3\frac{1}{3}$ minutes and upon phase correction and Fourier transform yield spectrum with signal-to-noise ratio in excess of 300:1 over the entire spectral region.

The sunset occultation spectra analyzed in this work were acquired from 38 km altitude during a balloon flight, conducted from Ft. Sumner, New Mexico (34.48° N; 104.22° W) on 25 September, 1993. The flight was exceptional in that a very clear troposphere allowed us to track the sun all the way down to the surface. Thus, the lowest tangent height was 4 km. A spectral resolution of 0.0075 cm^{-1} (66 cm maximum path difference) was employed at solar zenith angles up to 93° ($\sim$28 km altitude), at which point we switched to 0.015 cm^{-1} resolution to allow more rapid sampling, and thereby keep the tangent, point, separation of successive pairs" of spectra in the 2-3 km range. Each analyzed spectral pair (reverse and forward runs) therefore represents 100 or 200 seconds of observations.

Data Analysis

Data analysis proceeded by a 2-step approach. First, a Non-Linear Least-Squares (NLLS) fitting algorithm was used to determine the slant column abundances for each target gas in each spectrum. Then a linear equation solver was used to retrieve vmr profiles. The entire spectral fitting and retrieval process is then repeated using the new retrieved vmr profile as the initial guess.

Before analyzing any MkIV spectra a "high- sun" spectrum is computed by averaging the lowest airmass spectra acquired from a height of 38 km. Each individual spectra is then ratioed by the "high-sun" to eliminate solar absorption features and spectrometer continuum curvature which would otherwise lead to systematic offset, in the line of sight column.

Spectral Fitting

An initial atmospheric state (defined by the pressure-temperature and vmr profiles) is prescribed and used by a "forward model" to compute a spectrum. An "inverse method" then compares this spectrum with the one actually measured, and adjusts the prescribed atmospheric state to improve the match. The NLLS algorithm performs simultaneous adjustments to the gas abundances, continuum level, continuum tilt, and frequency shift to minimize the squares of the residual between the computed and measured spectrum. The error in the slant column determination is computed from the residuals, and includes contributions from

determination is computed from the residuals, and includes contributions from the covariances of the other fitted parameters, and uncertainty in the spectrum zero level.

PROFILE RETRIEVAL

The slant columns, together with the matrix of computed geometrical slant path distances, are then inverted, using the linear equation solver, subject to a derivative constraint to yield vmr profiles. The vertical separation of the retrieved vmr profiles was chosen to be 1 km, despite the tangent point spacing being 2-3 km. There are two reasons for this choice (i) compatibility with the forward model inputs, and (ii) not to degrade the high vertical resolution immediately below the balloon where the tangent point separation is small. The reported error in the retrieval of vmr represents the relative precision of the retrieval at the various levels. '1'11('s(' are the changes to the vmr that would change the slant columns by their one sigma uncertainties. Levels which lie close to the tangent altitudes tend to have smaller errors than those in between. Retrieved vmr values were allowed to go negative so as not to positively bias the profiles and hence the total fluorine. Generally, the negative retrieved vmrs are smaller than their uncertainties so that they are not statistically significant.

AUXILIARY DATA

The temperature profiles used initially in this exercise were radiosonde measurements compiled from the stations around the launch site. '1'hese were subsequently refined using vmr profiles of CO_2 derived from temperature-sensitive lines near 2390 cm^{-1}. These spectral lines provide temperature profiles accurate to within a couple of Kelvin. In general, the sensitivity of the fluorine absorptions used in this study to temperature are small and so the error in the final temperature profile is not a significant source of error in slant columns. The 11101 ('("111211" Spectral parameters used in the spectral fitting calculation were taken from the ATMOS compilation [*Brown et* al., 1 987] but incorporating recent improvements from the HITRAN linelist [*Rothman et* al., 1 '393]. Spectroscopic parameters for the fluorine species described in the present work are reproduced in Table 1. '1'he systematic error, in the retrieved burden, arising from using this spectroscopic compilation is

essentially due to uncertainties in absolute line strengths at 296 K and their temperature dependences. Changes in the former can be accounted for by a simple scaling of the gas burdens. However, a complete spectral fitting and vmr retrieval is necessary to incorporate corrections to the temperature dependence.

Other Gases

In addition to the fluorine species, spectral analyses were performed on many other gases including CO_2, N_2O, and N_2. Solar zenith angles of individual spectra were determined by constraining retrieved mixing ratios of CO_2 to be consistent with *in-situ* measurements [*Schmidt and Khedim, 1991*]. The retieval of a long-lived tracer like N_2O allow exacting studies of correlations amongst the many gases measured by MkIV and facilitates comparison with results of similar exercises from other instruments and models. An independent measure of the end-to-end analysis procedure was provided by N_2 retrieval using the lines near 2400 cm^{-1}. The retrieved values ranged between 0.77 and 0.82 having a rms deviation of only 1 % over the 20-35 km altitude range from the known value of 0.78. The systematic errors are largely due to pointing inaccuracies and uncertainties in the temperature profiles.

Results And Discussions

Fluorine Gases In The Stratosphere

In this section we describe briefly, for fluorine species listed in Table 1, the absorption features selected for spectral fitting and the retrieved vmr profile. While MkIV observations of the principal fluorine sources (CF_2Cl_2, $CFCl_3$, CHF_2Cl) and sink (HF) have been presented before [*Toon et al.,* 1989; *Sen et al.,* 1995], they will be further discussed to assert our capability to measure fluorine loading in the atmosphere.

CF_2Cl_2 (CIW-12)

CFC-1 2 was analyzed using the two Q-branches at 922 cm^{-1} and 1161 cm^{-1}. The spectroscopic parameters used in the analysis were derived from published high-resolution absorption cross sections [*Varanasi, 1992*]. These absorption cross sections were calculated from laboratory spectra acquired at atmospheric pressures and temperatures similar to those sampled by remote-sensing instruments.

Although the 1161 cm^{-1} region suffers from interference by O_3 and N_2O, its stronger absorption allows CFC-12 to be retrieved to slightly higher altitudes.

Figure 1 shows an example of an observed (diamonds) and calculated (solid line) spectrum used in the retrieval of CFC;-12. The retrieved vmr profile for all fluorine source gases measured by the MkIV is illustrated in Figure 2. The CFC;-12 approaches a tropospheric value of 500 pptv down to 5.5 km, the minimum altitude to which vmr profiles were retrieved.

$CFCl_3$ (CFC-11)

CFC-11 ranks second to CFC-12 in atmospheric abundance of anthropogenic gases. Due to the absence of sharp Q-branch-like features in the CFC-11 spectrum, the entire ν_4 band between 830-860" cm^{-1} has to be fitted simultaneously.

The spectroscopic parameters for the analysis were again derived from the published high-resolution absorption cross sections [*Varanasi*, 1992]. The result of a spectral fit and is shown in Figure 3. The interval is simultaneously fitted for CFC-11, HNO_3, CO_2, and H_2 0. The retrieval gives a tropospheric value of about 290 pptv, in agreement with *in-situ* measurements [*Kaye et al.*, 1 994].

CHF_2Cl (HCFC-22)

Concern over environmental consequences of CFC's in the atmosphere have resulted in their replacement with shorter-lived HCFC's of which HCFC-22 is currently the most abundant. The retrieval of atmospheric HCFC-22 profile is 1)21 sed on the anomalous $2\nu_6$ Q-branch at 829.05 cm^{-1}. The spectral interval is analyzed for the prominent HCFC-22 and O_3 using the spectroscopic compilation of *Brown et al.* [1 987]. The ability to detect and measure HCFC-22 is illustrated by the fitting (Figure 4) in which the residual is almost at the level of' spectrum noise. The vmr is very similar in profile to that reported earlier by ATMOS [*Zander et al.*, 1 992] but almost 89% higher in tropospheric absolute value. It reflects the growth of this gas at the Earth's surface and its transport into the stratosphere, as also reported by *Gunson et (L/.*, [1 994]. The tropospheric value of about 125 pptv is consistent with *in-situ* measurements.

$CF_2ClCFCl_2$ ((WC-I13)

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CFC-113 is another important fluorine-bearing, anthropogenic, tropospheric source gas measured by the MkIV. It exhibits several featureless, broad absorptions in the mid-infrared, the most easily measured being the ν_{10} band in the 804-830 cm^{-1} region. The spectroscopic parameters for CFC-113 and two interfering gases (HCFC-22, ClNO$_3$) were derived from published absorption cross sections [*McDaniel et al.*, 1991; *Varanasi*, 1992]. Additionally H$_2$O, CO$_2$, and O$_3$ were also simultaneously fitted to accurately characterize the computed spectrum. Figure 5 illustrates a typical spectral fit, the dashed line representing the absolute transmittance of CFC-113 alone. Despite contributing no more than 8% absorptance in the illustrated spectrum, and overlapping the R-branch of the HCFC-22 ν_4 band, CFC-113 can nevertheless be accurately quantified since the HCFC-22 can be unambiguously determined from its well isolated $2\nu_6$ Q-branch at 829.05 cm^{-1}. The retrieved vmr profile for CFC-113 is shown in Figure 2 and represents the first ever published using remote sensing techniques. The gas approaches a tropospheric value of 80 pptv, consistent with measurements reported in [*Kaye et al.*, 1994]. While its concentration at the ground is small ($\sim$80 pptv), CFC-113 nevertheless contributes $\sim$14% of the total tropospheric fluorine budget.

CF$_4$

CF$_4$ is an inert gas widely used for low-temperature refrigeration, as an insulator in electrical subsystems, and is also produced as a by-product of aluminum smelting. The chemical lifetime of CF$_4$ is extremely long and so it is expected to be well mixed throughout the troposphere and stratosphere.

CF$_4$ is analyzed in the MkIV spectrum by fitting both its Q-branch around 1283 cm^{-1} and the R-branch at 1285 cm^{-1}. In each case, the target gas is fitted along with N$_2$O, CH$_4$, and H$_2$O to minimize errors they might introduce. Figure 6 shows a fit to the broad Q-branch of CF$_4$ in a spectrum recorded for a tangent height of 26.37 km. Again, the absolute transmittance due to CF$_4$ alone is illustrated using dashed line. The derived vmr profile for CF$_4$ is shown in Figure 2. The gas has an almost constant profile ($\approx$52 pptv) from 20 km up. However, throughout the troposphere the profile exhibits a monotonic decrease from 1 00 pptv at 5 km to 52 pptv at the tropopause. The best estimate of atmospheric lifetime of CF$_4$ is more than 25000 years [*Ravishankara et al.*, 1993], far longer than the time scales

of mixing or meridional transport, thus making it well mixed globally. The large monotonic decrease of $\approx 50\%$ in vmr from the middle to the upper troposphere is unexplained and awaits further review of the spectral interval.

SF_6.

SF_6 is a trace gas produced entirely for use in high- voltage electrical and electronic equipment and has no known natural sources. The high chemical stability and long atmospheric residual time (>5000" years) has also allowed one to use SF_6 as a meteorological tracer. The gas is identified in the MkIV spectrum by its Q-branch at 947.9 cm^{-1} and can be retrieved over much of tangent altitude range in the September 1993 balloon flight.

The Q-branch of SF_6 is fitted in Figure 7 along with the more prominent CO_2 and H_2O absorption. The broad SF_6 absorption (947,7 - 948.0) cm^{-1}) is overlapped by a high ground-state energy CO_2 line (F;''=2416 cm^{-1}). However, the entire absorption is much wider than the CO_2 and thus can be clearly distinguished from it. The SF_6 vmr profile retrieved from the MkI V observations is shown in Figure 2. Our upper-tropospheric vmr of 3.8 pptv is consistent with the 1985 ATMOS measurements when the published global average exponential increase rate of 1 0.5%/yr is considered [*Rinsland et al.*, 1 990].

HF

HF is created in the stratosphere from the destruction of CFC's. It undergoes almost no further chemical changes and is lost from the stratosphere through a slow diffusion in to the troposphere and an eventual rainou t. HF was retrieved using three lines of its 1-0 transitions, as described in *Sen et* al., [1 995]. The lines are listed in 'I'able 1. The derived HF slant columns were a weighted mean of all three. Spectral fit to the HF R1 line is illustrated in Figure 8. The spectrum was recorded from an altitude of 37.4 km and at an astronomical solar zenith angle of 94.07°. The 0.015 cm^{-1} resolution spectrum was observed to be at a tangent height of 21.7 km. A H_2O line at 4039.25 cm^{-1} is the primary interfering gas and has been simultaneously fitted to minimize its impact on the HF. The vmr profile of both HF and COF_2 is reproduced in Figure 9. HF approaches a stratospheric value of 1.15 ppbv at 39 km, a value commensurate with recent ATMOS observations [*Zander et (L/j* 1994]. 'I 'he retrieved profile includes an

inflection at around 23-25 km altitude. As this feature is also present in all the long-lived trace gases retrieved (e.g. N_2O and CFC-12) it can be attributed to local transport effect and not some chemical changes in HF.

COF_2

COF_2 constitutes about one third of the entire inorganic fluorine abundance in the stratosphere making it the dominant temporary-reservoir of fluorine at the latitudes of MkIV observations. Formed from the break-down of CFC-12 and HCFC-22, COF_2 can further photolyze to form HF, the only known fluorine sink in the stratosphere. COF_2 is also an important intermediate in the decomposition of currently proposed alternate fluorocarbons. Its measurement allows understanding of chemical reactions following the breakup of anthropogenic gases in the stratosphere. The J 1 'I, MkIV spectra covers all the COF_2 absorption features observed in the laboratory, including those around 1938 cm^{-1} used by ATMOS for retrieval of the gas [*Zander et al.,* 1 994]. Retrieval performed using manifolds at 1938 cm^{-1}, Figure 10, were found to have better precision than the ones centered around 1234 and 1251 cm^{-1}. A weighted slant column abundance from all three spectral intervals was used in this study, although it differs from that obtained from the 1938 cm^{-1} interval alone, by only 4.4%±1.6%. The COF_2 profile in the mid-latitude stratosphere peaks at 31 km to a maximum value of 0.21 ppbv. The profile above the maximum decreases very smoothly with height. The vmr profile and value agrees well with ATMOS observations of 1992.

MID-LATITUDE FLUORINE ABUNDANCE

Total fluorine in the upper stratosphere results from the accumulation of the inorganic gases HF, CO FCl, and COF_2 as well as the long-lived organic species CF_4. As CF_4 is well mixed on a global scale and maintains its characteristic throughout the troposphere and stratosphere, the total budget is thus the sum of inorganic fluorine ([HF] + [COFCl] + 2*[COF_2]) plus the constant bias of CF_4.

The only inorganic fluorine species in the lower stratosphere not measured by the MkIV is COFCl. The lack of any discernible absorption signature of COFCl in solar-occultation infrared spectrum makes the gas impossible to measure. In the MkIV spectrum, the principal region of COFCl absorption (1850.1- 1 907.9 cm^{-1}) is dominated by spectroscopic signatures of the immensely more abundant gases

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O_3 and CO_2 making the fluorine species impossible to detect and quantify. The gas arises primarily from the photolysis of $CFCl_3$ in the lower stratosphere. Since COFCl is also the most easily photolyzed fluorine reservoir, its vmr falls off rapidly with ·increasing altitude [*Kaye et d.*, 19{)1]. The vmr profile of COFCl used in this study, Figure 9 (dashed line), is a 2-I) model calculation and its contribution to the mid-latitude inorganic fluorine budget is at most 6% in the altitude range below 30 km. Details of' the 2-I) model and some its results have been described elsewhere [*Sen et (11.*, 1995, *Kaye et al., 1 991]*. The 2-1) model calculation was carried out over the period 1970-201 (), with source gas conditions at the ground updated each 1 year based on WMO reports. The COFCl vmr profile represents the conditions in September 1993 at a latitude of $35°$ N (time and latitude of MkIV sunset). The profile peaks to a value of 83 pptv at an altitude of 25 km. COFCl practically disappears above 33 km and plays n o role in the inorganic fluorine budget at greater heights.

The sum of inorganic fluorine and its **sources** in illustrated in Figure 11. The use of N_2 (), in place of altitude or pressure, allows a more useful illustration of fluorine (organic, inorganic, and total) mixing ratio profiles by removing any transport-induced folds in the individual profiles. Retrieved volume mixing ratio profiles for all fluorine species measured by the MkIV is tabulated in ~'able 2. The profile for COFCl is derived from the 2-1) model calculations. The vmr profile in the last column is the fluorine-number weight ed sum of all inorganic sinks and its organic **sources** (excludes CF_4 and SF_6). The mean total inorganic fluorine above 35 km, measured by MkIV, is 1.34 ppbv and is commensurate with recent ATMOS observations [*Zander et al.*, 1994]. Above 35 km the total inorganic budget is accounted for by HF and COF_2 alone. The inorganic fluorine budget is also in agreement with the mean tropospheric value (excluding CF_4) for 1987-1988, when a 5.2% per year increase in fluorine loading is added to the 1.32 ppbv reported for 1986 [*WMO*, 1988]. This indicates a 5-6 year transport time for the fluorine in lollg-lived source gases, released at the ground, to 1)e observed at 40 km. The mixing time is in good agreement with ATMOS results [*Zander et al.*, 1994] from˙ their analysis of long-lived anthropogenic source gases and the CO_2 vmr measurements of *Schmidt and Khedim* [1991]. *Hall and Prather* [1993] modeling an ensemble of CO_2 airmasses of different ages computed a mean delay of 4 years

between the parcel's characterization in the troposphere and at 30 km. The model value is in reasonable agreement with Mk V observations when considering the altitude differences and the caveat that the computed mean age is valid only for CO_2 concentration varying linearly with time.

Our measured organic fluorine budget at the lowest tangent altitude was observed to be 1.88 ppbv. On the basis of tropospheric measurements synthesized by *WMO* 1991], the total concentration of fluorine containing anthropogenic gases (CF_2Cl_2, CFC_3, CHF_2Cl, $CF_2ClCFCl_2$, $CBrClF_2$, $CBrF_3$) was 1 58 ppbv in 1990 and increasing 5.2% per year. The 993 measurements by MkIV are therefore good agreement with tropospheric measurements in 1990 when he rate of increase is factored in.

The fluorine budget from the 2-D model calculation is over-laid o t e Mk V results in Figure 12. The time-dependent model runs were performed for latitude and time encom assing the September 993 MkIV balloon flight. The model run for Septem er 1993 was i ni ialized wi h source CFC's and I CFC's emissions characteristic detailed in *WMO* [1991] and the tota fluorine (excluding CF_4) of 1.77 ppbv is consistent with MkIV observations. Summing up he inorganic fluorine above 35 km the model predic s a value of about 1.32 ppbv, in good agreement with MkIV observations. Further, comparing the time evolution of inorganic fluorine at 60 km (HF and COF_2) to the organic source concentrations used as yearly input into the model, a mean age of 5-7 years is derived for transport i to the pper stratosphere. This is i excellent agreement with resu ts from the current study and hat pu lished from analysis f ATMOS easurements [*Zander et al.*, 1994 Figure 12 also demonstrates the ight q tan i ative relation between fluorinate source gases released at he ground and the norgan c fluorine udget measured above 35 km. t clearly contradicts earlier the hypothesis that intense volcanic eruptions inject large amounts of 1F into the stratosphere [*Symonds et al.*, 1978]. The gradients of both the measurements and the model predictions illustrated in Figure 12 are greater than - mostly ecause HF has a tropospheric oss due to rainout, eliminating some of the   orine before it ever reaches the upper stratosphere. The time lag of fluorine in going from source o si k is also a contri n or, but is ess of a effect tha the rainout.

Summary

The study has dealt with determining the inorganic fluorine budget in the stratosphere using high-resolution infrared solar observations of CF_2Cl_2, $CFCl_3$, CHF_2Cl, $CF_2ClCFCl_2$, CF_4, SF_6, HF, and COF_2 from high-altitude research balloon. These species comprise 94-99% of total fluorine, depending on altitude. This is the first time all of these species have been measured simultaneously in the same spectrum, eliminating uncertainties which arise if the different gases are measured in different locations (e.g. *Zander et al.*, 1992). The mean total inorganic fluorine in September 1993 was 1.34 ± 0.06 ppbv over the 35-40 km range and 1.88 ± 0.26 ppbv at 5 km. Within the uncertainties of MkIV measurement, the inorganic fluorine budget is consistent with tropospheric values in 1987-1988 confirming the conservation of total fluorine throughout the stratosphere. The observed inorganic fluorine budget is in agreement with ATMOS measurements and 2-D model predictions demonstrating that the latter reasonably represents both the chemistry and transport of fluorine source, reservoir, and sink species.

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Fig. 1. CF_2Cl_2 (CFC-1 2) spectral fit at a refracted tangent altitude of 11.3 km. CO_2 and H_2O were simultaneously fitted along with CFC-12. [In this and all subsequent spectral plots, the diamond shows the measured spectral values, while t he solid line shows the fitted calculation. The dashed line shows the spect rum that would result from t a r g e t gas alone. The "residuals" enlarge the differences between the measured and calculated spectra.]

Fig. 2. Retrieved vmr profiles of organic fluorine source gases,

Figure 3. $CFCl_3$ (CFC-11) spectral fit at a refracted tangent altitude of 13.9 km. HNO_3, H_2O, and CO_2 were simultaneously fitted along with CFC-11.

Fig. 4. CHF_2Cl (HCHC-22) spectral fit at a refracted tangent altitude of 11.3 km. O_3 was simultaneously fitted along with the HCFC-22 Q-branch.

Fig. 5. $CF_2ClCFCl_2$ (CFC-113) spectral fit at a refracted tangent altitude of 8.8 km. HCFC-22, $ClNO_3$, H_2O, CO_2, and O_3 were simultaneously fitted along with CFC-113. Despite the CFC-113 absorptance being no more than 8%, and overlapping considerably with the HCFC-22 absorption, the gas can be fitted well due to the precision of results achieved in retrieving HCFC-22 from its 829.05 cm^{-1} line (Figure 4).

Fig. 6. CF_4 spectral fit at a refracted tangent altitude of 26.4 km. N_2O and CH_4 were simultaneously fitted along with the broad-band absorption by CF_4.

Fig. 7. SF_6 spectral fit at a refracted tan gent altitude of 19.5 km. CO_2 and H_2O were simultaneously fitted along with SF(; , The broad SF_6 absorption (dashed line: 947.7-948.0 cm^{-1}) has its peak located at 947.94 cm^{-1} overlapping a high-ground state energy (E $=2416$ cm^{-1}) CO_2 line.

Fig. 8. HF spectral fit at a refracted tangent altitude of 21.7 km. H_2O at 4039.25 cm^{-1} was simultaneously fitted along with the HF R 1 absorption at 4038.96 cm^{-1}.

Fig. 9. Retrieved vmr profiles of inorganic fluorine gases. COFCl profile (dashed line) is a time-dependent 2D model calculation performed for the time and latitude of MkIV observations.

Fig. 10. COF_2 spectral fit at a refracted tangent altitude of 30.4 kin. CO_2 and $H_2 0$ were simultaneously fitted along with COF_2. The ten nearly unblended manifolds of COF_2 are located at 1936.26, 1936.68, 1937.10, 1937.52, 1938.94, 1938.36, 1938.77, 1939.19, 1939.62. and 1940.02 cm^{-1},

Fig. 11. Total fluorine budget measured by MkIV at 35° N in September 1993. The profiles correspond to budgets of fluorine (Table 2) incorporating six of the measured gases (CFC-12, CFC-11, HCFC-22, CFC-113, HF and COF_2) and a gas (COFCl) from the 2-D model.

Fig. 12. Total fluorine in the inorganic species versus the organic sources. The figure demonstrates the tight quantitative relation between fluorinated source gases released at the ground and the inorganic fluorine budget measured above 35 km.

'J'able 1. Spectroscopic Interval and Parameters Used in Present Analysis.

Gas	Interval (m"')	Σ(strength) (cm.molec^{-1})	fIalf-Width (cm^{-1}.atm^{-1})	'ζ" (cm^{-1})
CF_2Cl_2	92 1.80± 1.80	8.040X" 10^{18}	0.055	range
CF_2Cl_2	1160.9(H 0.75	3.790X10'"'"	0.030	range
$CFCl_3$	845.90± 31.50	6.050X 10'"^{7}	0,050	range
CHF_2Cl	829.05± ().S()	2.796 x10^{-19}	0.030	230.0
$CF_2ClCFCl_2$	816.60± 28.80	5.484 X1O'"7	0.050	range
CF_4	1 283.00.! I .00	5.341 x10^{-17}	0.080	range
CF_4	1285.55± 1.40	2,690 x10^{-17}	0.080	range
SF_6	947.95 ±0.75	1.910 X10"9	0.050	range
HF	3877.72%0.15	1.888x10^{-18}	0.090	123.3
HF	4039.96± 0.3()	2.369 x10^{-x}	0.089	41,1
Ill'	4109.95fl o. 15	1.585 x10^{-18}	0.050	246.4
COF_2	1234.25 ±0.33	1.495 x10^{-18}	0,084	rail.gc
COF_2	125 1.00±0.80	2.627x10^{-18}	0,084	range
COF_2	1938.15±2.04	4.121 x10^{-18}	0.084	range

Table 2. MkIV stratospheric fluorine budget for 35°N, September 1993.

				Sources						Reservoirs			Sink	
Height km	Temp K	Pres hPa	N_2O ppbv	CF_2Cl_2	$CFCl_3$	CHF_2Cl	F_3C_{l3}	C_{l4}	F_6	COFCl pptv	COF_2 pptv	HF pptv	Total pptv
5.52	267.03	316.2	342±3	2 U . 1	6 f I E	i 9 .	1 1	% X	1.0±1.3	0.1	49.4±14.	4.1±16.	1882.6±269.
6.5	262.37	454.24	337.0±15.	509.0±16.	281.0±9.3	125.6±26.	70.4±10.	106.W26.	1.3±1.0	0.1	40.19.3	1.734.6	1843.5±71.5
7.5	256.72	398.31	330.0±16.	501.0±28.	280.0±15.	121.1±26.	72.4±7.5	98.0±18.	1.9±0.8	0.2	27.1±6.9	-1.4±9.6	1794.4±82.8
8.5	247.88	348.05	323.0±14.	493.0±24.	279.0±13.	117.3+2s.	74.6±7.1	90.033.	2.7%.7	0.3	14.1±6.0	-4.1±8.3	1747.7579.2
9.5	239.03	302.56	315.0+11.	486.0±15.	278.0±8.9	114.9±8.9	76.2±7.0	83.3±10.	3.4±0.6	0.4	3.7±5.6	-4.s5.0	1711.3±43.4
10.5	233.65	261.93	310.0±14.	485.0±25.	278.0±14.	114.9±16.	76.5S.S	78.6±8.5	4.1±0.5	0.4	-3.0±5.3	-3.1±9.1	169 8.7±65.8
11.5	227.43	226.06	308.0±9.4	491.0±15.	282.0±8.8	116.2±15.	75.4±6.3	75.8±6.6	4.6±0.4	0.5	-6.4±4.4	-1.25.5	1709.1±48.4
12.5	220.62	194.14	309.0±11.	503.0±20.	292.0±11.	11s.757.4	72.9±6.7	74.1±6.3	4.73.4	0.s	-7.6?4.5	-1.8±7.4	1738.0±49.7
13.5	213.49	165.97	310.BI2.	516.0±23.	304.0±12.	122.0±15.	6s.s?6.5	72.13.6	4.733.4	1.3	-7.5?4.7	-4.339.1	1768.4±60.9
14.5	205.95	141.15	307.0±7.1	520.0±12.	310.0±7.3	125.8±8.8	62.357.1	67.6*4.6	4.6±0.3	4.4	-6.924.5	-6.1±4.8	1773.0±38.6
15.5	199.90	119.26	299.0±12.	514.0±24.	308.0±13.	128.5±11.	53.1±7.5	60.3±5.2	4.43.4	S.4	-5.95.0	-4.4±10.	1744.5±60.6
16.5	199.51	100.62	293.0±7.8	505.0±16.	303.0±8.6	126.8±15.	44.4±8.2	52.S?4.2	4.353.3	8.6	-3.3*4.9	1.653.2	1703.432.5
17.5	201.32	84.92	290.0±9.0	499.0±18.	294.0±9.8	122.1±7.3	41.4?7.2	47.8±4.5	4.3±0.3	11.1	2.8±5.5	12.453.6	1689.5±47.6
1s.5	203.21	71.79	285.0±12.	482.0±25.	272.0±13.	115.7±16.	46.4±6.9	45.7±5.5	4.250.4	17.8	13.9±6.S	36.0±14.	1688.2±67.1
19.5	207.37	60.84	269.0±5.6	443.0±12.	232.0±6.5	105.7317.	55.7*7.1	46.0±4.4	4.1±0.4	25.3	31.057	87.5±10.	1671.3±50.1
20.5	211.92	51.74	235.0±7.2	369.0±15.	172.0±7.5	97.7? 10.	62.7±8.0	47.7?4.3	3.99.4	33.1	53.7?7.0	185.0±12.	1619.0±47.7
21.5	214.S5	44.14	197.0±6.5	288.0±14.	109.0±7.1	91.9±15.	62.5±10.	49.9±4.3	3.6±0.4	45.5	79.5±7.5	314.0±14.	1574.9±55.3
22.5	217.03	37.72	171.0±4.5	239.0±9.8	59.s5.5	78.2±16.	55.8±11.	51.8±4.0	3.350.4	5s.1	103.0±7.8	420.0±13.	1545.8±54.2
23.5	21S.71	32.28	162.0±6.7	227.0±15.	30.2?7.0	63.5±18.	46.4±10.	53.0±4.5	3.1±0.5	69.5	122.0±9.0	470.0±8.	1533.8±61.7
24.5	220.30	27.66	159.0±2.9	226.0±6.7	16.1±5.6	49.1±9.	38.9±0.	53.9±3.5	3.1±0.5	7s.9	136.0±8.8	478.0±13.	1511.9±55.2
25.5	221.S0	23.73	153.0±5.7	212.0±13.	11.7±6.6	49.0±21.	37.3±11.	54.7?4.2	3.2±0.6	S3.4	148.0±10.	489.0±19.	1514.0355.s
26.5	223.31	20.3s	143.0±2.8	183.0±6.9	11.55.9	59.2523.	42.3A11.	55.3?3.4	3.3±0.6	83.1	160.0±10.	519.0±16.	1545.0%4.7
27.5	224.14	17.51	132.0±4.4	149.0±10.	11.0±6.1	67.2±24.	51.4±13.	55.3±3.8	3.6±0.6	76.S	174.0±12.	565.0±20.	15s7.3?73.0
2s.5	224.86	15.06	117.0±2.6	116.0±7.1	8.8±7.6	62.452S.	59.8±15.	54.8±3.3	3.8±0.7	73.2	190.0±12.	625.0±17.	1613.1379.1
29.5	226.S9	12.96	98.2±3.7	89.1?9.5	5.4±8.0	44.3±32.	59.6±18.	54.7±3.8	3.7±0.8	49.3	204.0±12.	695.0±23.	1603.3±91.9
30.5	229.23	11.18	80.1±3.4	70.0±9.3	2.0±6.5	22.8±3s.	47.1±26.	54.9±3.5	3.5±0.8	33.S	212.0±14.	751.0±24.	1537.7±110.
31.5	230.82	9.65	67.7±3.2	57.4±9.0	-0.456.0	5.5±32.	27.1±42.	55.2±3.6	3.0±0.9	18.6	213.0±17.	787.0±23.	1438.4±147.
32.5	230.0S	8.33	5s.25.0	47.3514.	-1.427.6	-4.9?23.	6.5±60.	55.4±5.3	2.4±1.0	9.6	209.0±18.	830.0±39.	1360.65195.
33.5	229.33	7.19	50.2±3.1	37.1*11.	-1.4±8.3	-7.3±34.	-8.3±73.	55.5±4.0	1.9±1.1	2.s	205.0±16.	871.0±32.	1317.1±235.
34.5	232.S1	6.21	41.3±1.9	23.1±7.1	-0.8±8.3	-11.6±37.		55.4%.7	1.5±1.3	0.9	202.0±14.	911.0±21.	1338.1±83.5
35.5	237.23	5.3s	31.3?2.5	5.8±10.	0.1±8.0	-19.9±40.		55.0±3.8	1.4+1.5	0.2	202.0±16.	976.0±34.	1352.1±95.1
36.5	239.96	4.67	24.6?0.7	-8.9±7.3	0.8±6.9	-25.3266.		53.8±2.4	1.631.9	0.1	198.0±19.	106O.WI3.	1388.5±139.
37.5	240.90	4.06	22.4±0.6	-15.8±11.	1.4?5.6	-29.4*66.		51.8±3.7	2.1±2.4		188.0±26.	1120.0±19.	1407.0±145.
3s.5	242.ss	3.53	17,4?2.3	-16.2±18.	1.526.2	-55.6±71.		49.7±6.2	2.9±2.9		176.0±34.	1050.0±5 1.	1259.9±169.
39.5	250.50	3.0s	14.253.5	-12.S?27.	1.4±8.3	-60.3577.		48.0±9.3	4.0±3.3		164.0±43.	988.0±75.	1171.2±199.

VMR Profiles

$\chi = 95.14°$ $T = 13.9°$ km $\sigma_{rms} = 0.63\%$ $\int \rho(CCl_3F)$ $dz = 6.5°3 \pm 0°5 \times 10^{14}$ molec.cm^{-2}

Transmittance

Residual ($\Delta T \times 100$)

Frequency (cm^{-1})
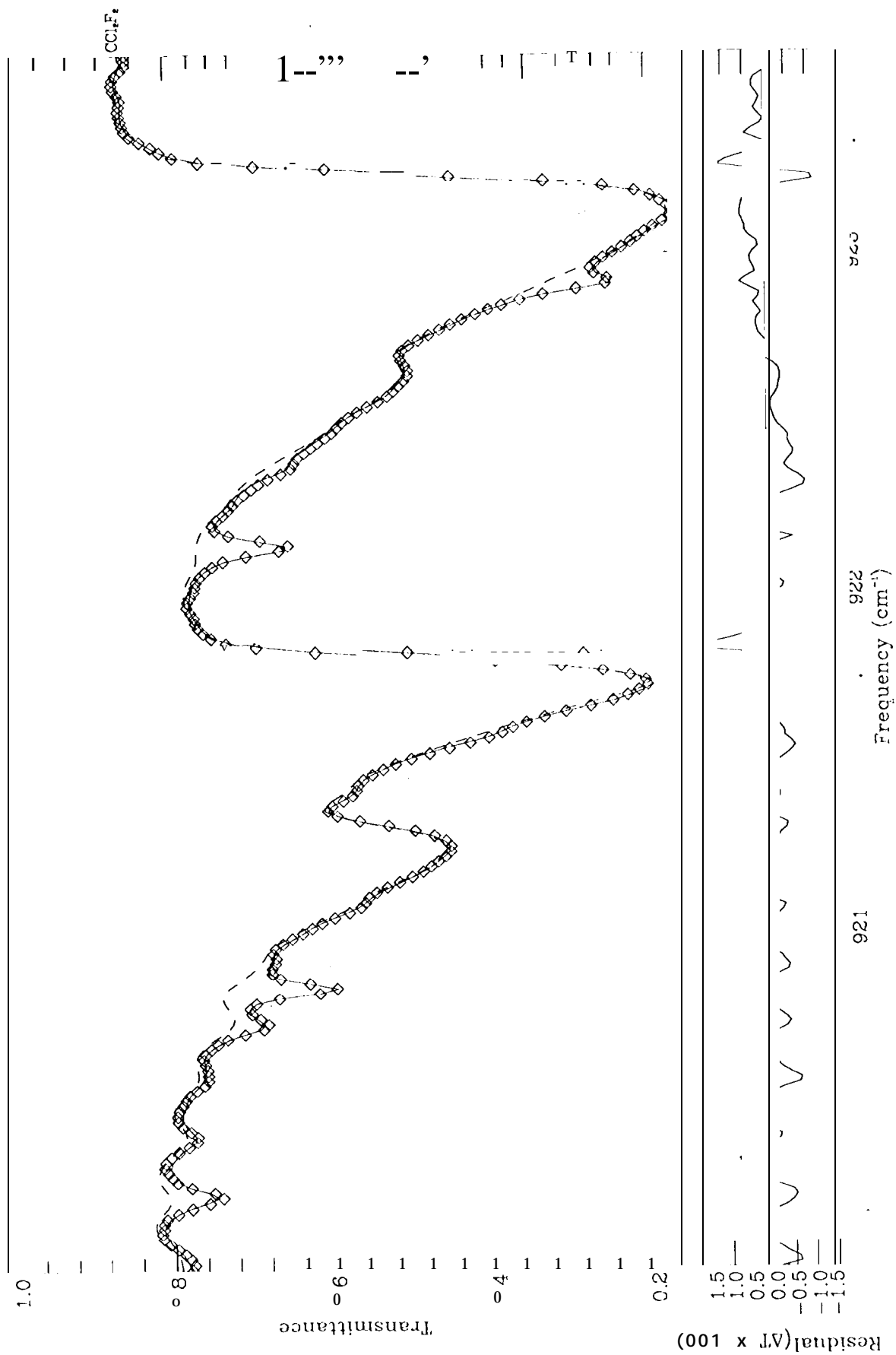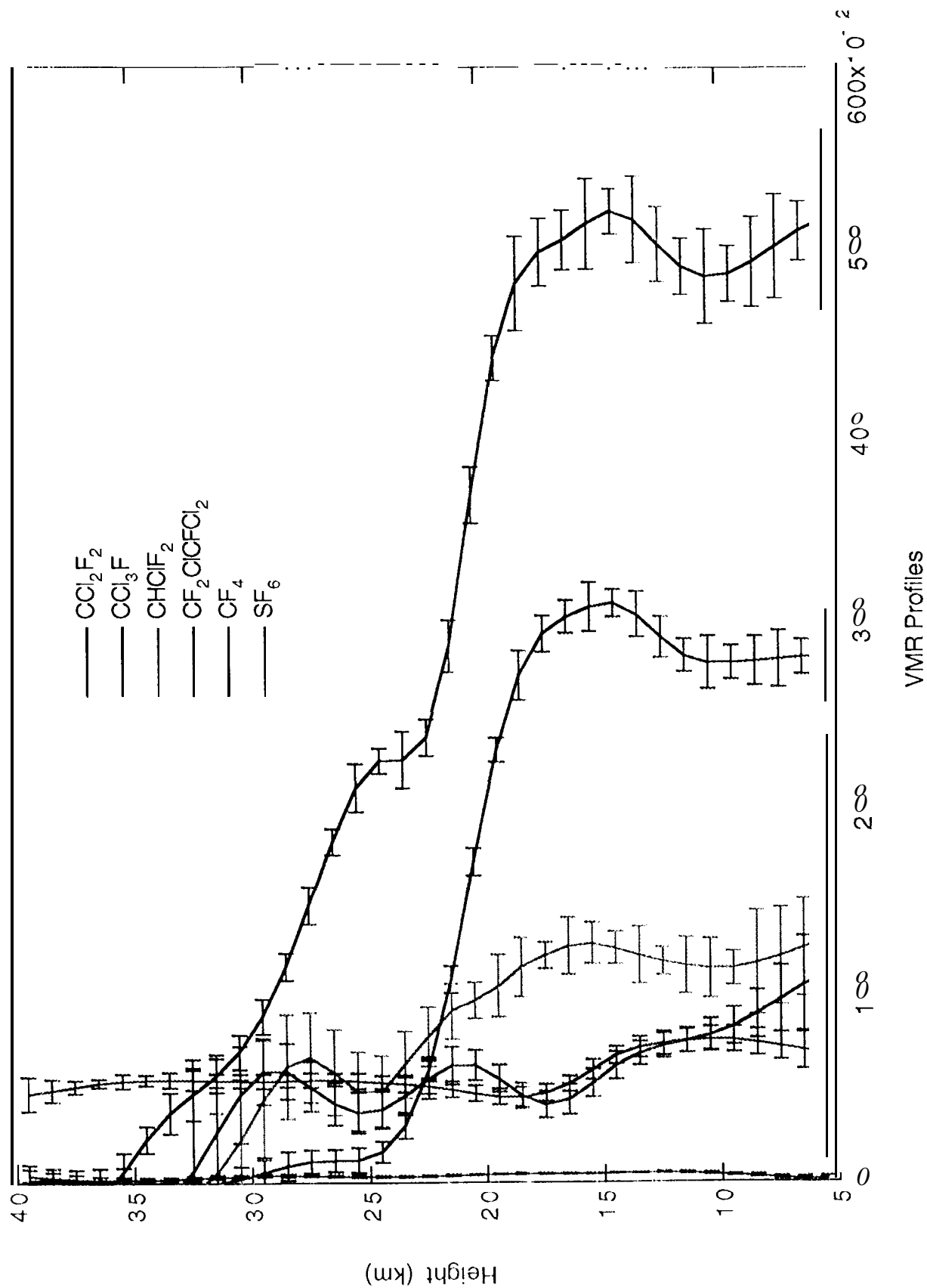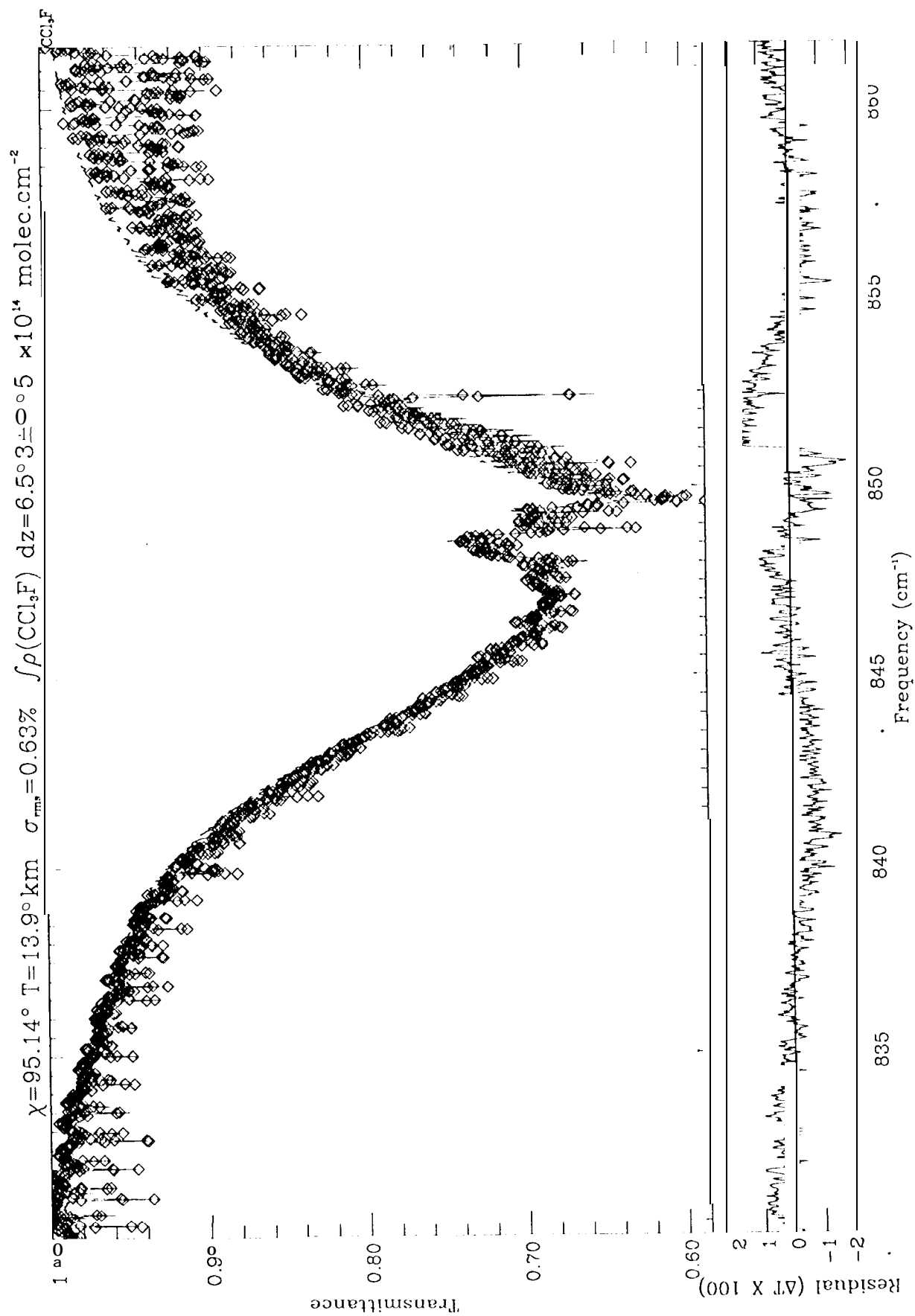
CHClF₂
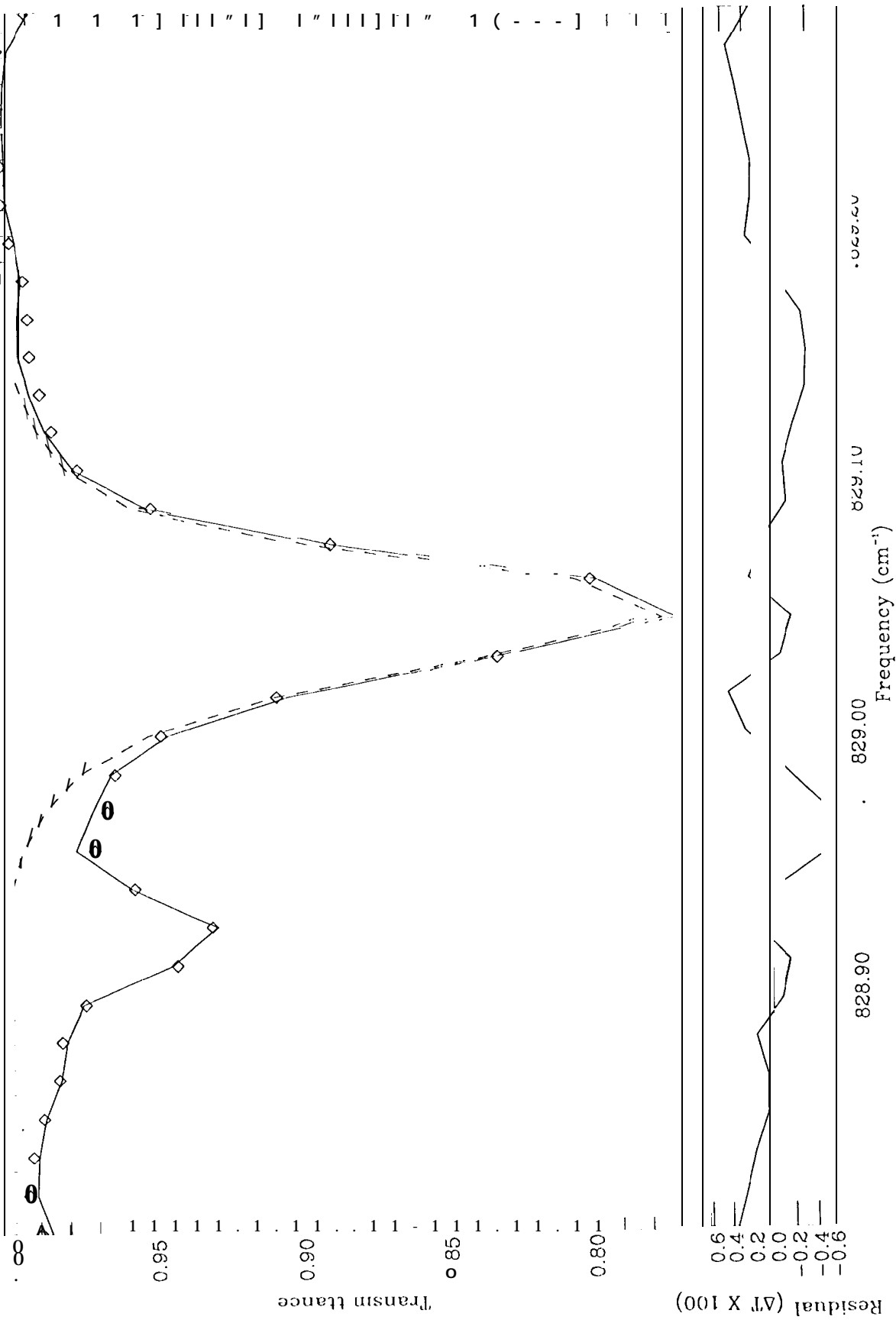
$\chi=95.85°$ T= 8.78km $\sigma_{rms}=1.34\%$ $\int\rho(CF_2ClCFCl_2)$ dz=4.931±0.160x10^{14} molec.cm^{-2}

$\chi = 93.39°$ $T = 26.41km$ $\sigma_{rms} = 1.07\%$ $\int \rho(CF_4)$ $dz = 2.646 \pm 0.083 \times 10^{13}$ molec.cm^{-2}

CF$_4$

Transmittance

Residua ($\Delta T \times 100$)

Frequency (cm^{-1})

$\chi=94.37°$ $T=19.51$km $\sigma_{rms}=0.17\%$ $\int\rho(SF_6)$ $dz=6.262\pm3.400\times10^{12}$ molec.cm^{-2}

$\chi=94.06°$ T=21.74km $\sigma_{rms}=0.15\%$ $\int\rho$(HF) dz=5.347 ± 0.066x10^{14} molec. cm^{-1} HF

$\chi = 92.69°$ $T = 30.44 km$ $\sigma_{rms} = 0.22\%$ $\int \rho(COF_2) dz = 5.965 \pm 0.260 \times 10^{13}$ molec. cm⁻¹

Approx. Height (km)

$HF + 2^*COF_2 + COFCl$

$2^*CCl_2F_2 + CCl_3 + 2^*CHCIF_2 + 3^*CF_2CICFCl_2$

MkIV 993
ATMOS 1992
GSFC 2D Model